Zigzag Ligands for Transversal Design in Reticular Chemistry: Unveiling New Structural Opportunities for Metal-Organic Frameworks

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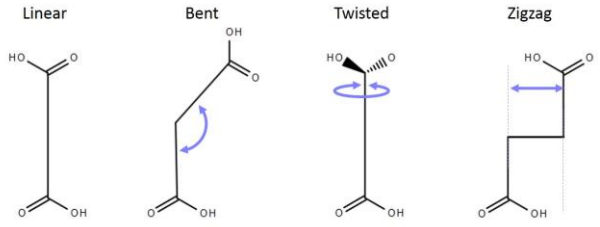
ABSTRACT: Herein we describe the topological influence of zigzag ligands in the assembly of Zr(IV) metal-organic frameworks (MOFs). Through a transversal design strategy using reticular chemistry, we were able to synthesize a family of isoreticular Zr(IV)-based MOFs exhibiting the **bcu** – rather than the **fcu** – topology. Our findings underscore the value of the transversal parameter in organic ligands for dictating MOF architectures.

Metal-organic frameworks (MOFs) are a revolutionary class of materials constructed from metal ions/clusters and organic ligands that link together via self-assembly.[1] Marrying the richness of both organic and inorganic chemistries, MOFs have spread widely to many fields over the past two decades,[2] including in potential solutions for urgent problems such as energy use and environmental protection.[3] They are also relevant to applications such as sensors,[4] catalysts,[5] drug-encapsulation agents[6] and separation agents.[7]

Although MOFs offer seemingly limitless possibilities for self-assembly and, consequently, nearly infinite structural diversity, the methods for their synthesis remain ripe for optimization and expansion. Various approaches have been developed for synthesis of MOFs with desired structural (topology, pore size and shape) or functional properties.[1,8] Beyond classical trial-and-error approaches, researchers have also devised rational design strategies, including use of secondary building units[8a,b] and molecular building blocks (MBBs);[9] pillaring strategies with dicarboxylate-based or dipyridyl-based ligands;[10] post-synthetic modifications (ligand and/or metal exchange);[11] ligands with multi-isophthalic moieties;[12] supermolecular building blocks and layers;[10a,13] and pre-formed clusters.[14]

MOFs can be assembled from organic and inorganic MBBs that are linked in two or more directions, which leads to discrete, one-, two- or three-dimensional geometric assemblies with various topologies. The reduction of MBBs into purely geometric figures by connecting their points of extension enables today's molecular architect to put aside strictly chemical considerations and evaluate first-hand the geometric compatibility of the available building blocks. This reflection was made possible through extensive work by O'Keeffe, Yaghi and co-workers from the late 1990's[8a,c,15] which ultimately led to the creation, in 2008, of the Reticular Chemistry Structure Resource database.[16]

Scheme 1. Four Different Geometries for Dicarboxylic Ligands.



The majority of the most regular (edge-transitive) possible topologies[15e,f] have already been observed in MOFs. Researchers have extensively studied the assembly of linear ligands with various metals, obtaining prototypical MOFs such as MOF-5 (**pcu**),[15a] MIL-88 (**acs**)[17] or UiO-66 (**fcu**).[18] Use of triangular (**tbo**, **pto**, **the**, etc.),[15c,19] square/rectangle (**ftw**, **soc**, **scu**, **csq**, etc.)[20] and tetrahedral organic MBBs (**pts**, **flu**, etc.) leads to other edge-transitive networks.[21] Although topology has been proven to be a very powerful design tool, it has the particularity to reduce both organic and inorganic MBBs to single nodes or, in the case of augmented networks (**net-a**), to geometric figures delineated by their points of extension, in which the directionality of the connections is not addressed. Hence, all 2-connected ligands (Scheme 1), including bent isophthalic acid, are systematically reduced topologically to single lines.[22]

However, there are numerous reports demonstrating that the angle in bent ligands strongly influences the assembly of metal-organic polyhedra[13d,23] _ENREF_47 and MOFs.[24] Another point regarding use of linear ligands is that deliberate incorporation of steric hindrance adjacent to a given functional group can force it to tilt away from its preferred orientation, resulting in a *twisted ligand* (Scheme 1), which

in turn provides access to topologies that are generally not easily accessible.[25] Finally, although a few isolated structures with *zigzag ligands*[26] or 3-connected ligand with broken collinearity[27] have been reported, to the best of our knowledge, there have not yet been any reports on the potential use of their unique shape for rational design of MOFs.

Here we provide the first-ever report on the use of zigzag ligands to create isoreticular Zr-**bcu**-MOFs. By employing zigzag ligands, we anticipated the introduction of a transversal parameter in reticular chemistry. The shape of these ligands can be defined by four main geometric parameters (Figure 1a): height (*h*); width (*w*); carboxylate-to-carboxylate distance (*c*-*c*), which is equal to $(h^2+w^2)^{1/2}$; and angle (α), which is defined by *c*-*c* and *h* and is equal to arctan (*w*/*h*). Therefore, unlike the use of linear ligands, which can only be made taller or shorter (by adjusting the height; see Figure 1), our transversal reticular chemistry enables also stretching of the ligand in the transversal direction, varying the width (*w*, Figure 1). By breaking the collinearity of the carboxylate binding directions, our approach enables topological possibilities different from the default ones.

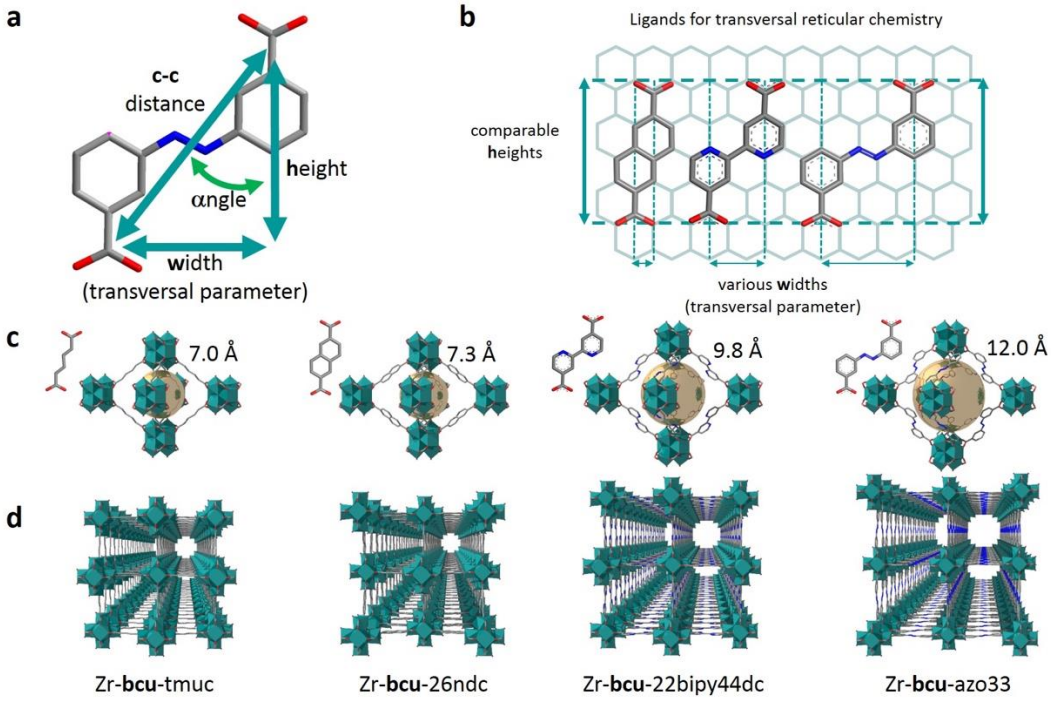


Figure 1. a) Characteristic distances and angle in zigzag ligands. b) Schematic of transversal reticular chemistry, showing three ligands with comparable height and variable widths. c) Representation of the cages associated with the structurally distinct MOFs Zr-**bcu**-tmuc, Zr-**bcu**-26ndc, Zr-**bcu**-22bipy44dc and Zr-**bcu**-azo33. d) Structural view of the MOFs Zr-**bcu**-tmuc, Zr-**bcu**-26ndc, Zr-**bcu**-22bipy44dc and Zr-**bcu**-azo33 along the *c* axis.

To begin exploring transversal reticular chemistry, we chose to work with *trans*,*trans*-muconic acid (tmuc), a zigzag ligand with a height of 5.8 Å and a width of 2.1 Å (Figure 2a). Reaction of tmuc and $ZrCl_4$ in DMF and trifluoroacetic acid at 120 ºC for 3 days afforded colorless crystals suitable for single-crystal X-ray diffraction (SCXRD). SCXRD analysis (performed on the XALOC beamline of the ALBA synchrotron[28]) revealed the formation of a 3D network of formula $Zr_6O_4(OH)_4(tmuc)_8(H_2O)_8$ (hereafter called Zr-**bcu**-tmuc), which crystallizes in a tetragonal system. As commonly observed in Zr(IV)-based MOFs, the inorganic building unit in Zr-**bcu**-tmuc is the ubiquitous $Zr_6O_4(OH)_4(OOC)_{12-x}(H_2O)_{2x}$ (x = 4) hexanuclear cluster. In this framework, each of these units is connected to eight others through eight bridging zigzag tmuc ligands adopting overall an 8-connected, **bcu** topology (Figure 1c,d).

If most Zr(IV)-based MOFs built up from dicarboxylate linear ligands adopt the **fcu** topology, the use of a zigzag ligand permitted deviation from it and favored the formation, somewhat unexpectedly, of the **bcu** network. Interestingly, there are previous reports that tmuc, when acting as a linear ligand, can also form the standard Zr-**fcu**-MOF (Figure 2).[14] Here, we would like to mention that the **bcu** topology actually derives from the **fcu** topology: it consists of an **fcu** network in which one-third (four out of 12) of the bridges are absent, resulting in a similar face-centered-cubic packing in which the connectivity of the 12-c nodes is reduced to 8 (Figure 2c). Thus, we attributed the topological deviation from **fcu** to a **bcu** to the zigzag conformation of tmuc. Indeed, inspection of the octahedral cage of Zr-**bcu**-tmuc compared to that from Zr-**fcu**-tmuc[14] reveals that the zigzag conformation of tmuc ligands in Zr-**bcu**-tmuc does not match the perfect alignment of the clusters in the structure (Figure 2b, purple arrows). Moreover, although the distances between the clusters bridged by tmuc ligands in Zr-**bcu**-tmuc (15.0 Å) are comparable to that in Zr-**fcu**-muc (14.6 Å), the cluster-cluster gaps that are not filled by tmuc in the former appear to be too wide (16.8 Å) to accommodate additional tmuc ligands. These unoccupied ligand "voids" in Zr-**bcu**-tmuc create 1D channels along the *c* axis whose pore size was estimated to be 7.0 Å (Figure 1d). In light of these apparent voids and free channels in Zr-**bcu**-tmuc, we evaluated its porosity by measuring its N_2 sorption at 77 K, obtaining values of 640 m^2/g for BET area and 0.27 cm^3/g for total pore volume (Figures S19, S20).

A detailed trigonometric study of the Zr-**bcu**-tmuc crystal structure confirmed that formation of this MOF is indeed governed by both the height and the width of the zigzag ligands (Figures S13-S18). From this study, we estimated their contribution to the cell parameters as follows:

$$ \approx \frac{2(+)}{} \cos(43 -) + 8.7$$

$$ \approx 2 + \frac{}{} \sin(43 -) + 13.1$$

Consequently, we reasoned that in addition to the classical elongation parameter (height [*h*]) used in reticular chemistry, the transversal parameter (width [*w*]) of the zigzag ligands could be exploited to construct a family of isoreticular Zr-**bcu** MOFs. Indeed, the above equations suggest that, for a set of zigzag ligands having a similar width, the effects of *h* on the cell parameters should follow the same trend as in classical reticular chemistry; that is, as the height of the ligand increases, so should the cell parameters (Figure S18). However, for a set of zigzag ligands of similar height, the transversal parameter reveals its influence on the cell parameters: thus, as the width increases, the *a* and *b* axes (*i.e.* the parameters that define the channel diameter) increase, whereas the *c* axis (*i.e.* the cluster-cluster distance along *z*) decreases (Figure 3).

To confirm this hypothesis and to illustrate the power of transversal reticular chemistry, we carefully selected three additional ligands of similar height (≈ 7.9 Å) but increasing width: 2,6-naphthalene dicarboxylic acid (26ndc; *w* = 1.1 Å), 2,2'-bipyridine-4,4'-dicarboxylic acid (22bipy44dc; *w* = 3.7 Å) and azobenzene-3,3'-dicarboxylic acid (azo33; *w* = 5.7 Å). We reasoned that combining such features in a series of isoreticular MOFs would enable inhibition of the height effect, thereby providing the first-ever case of purely transversal reticular chemistry.

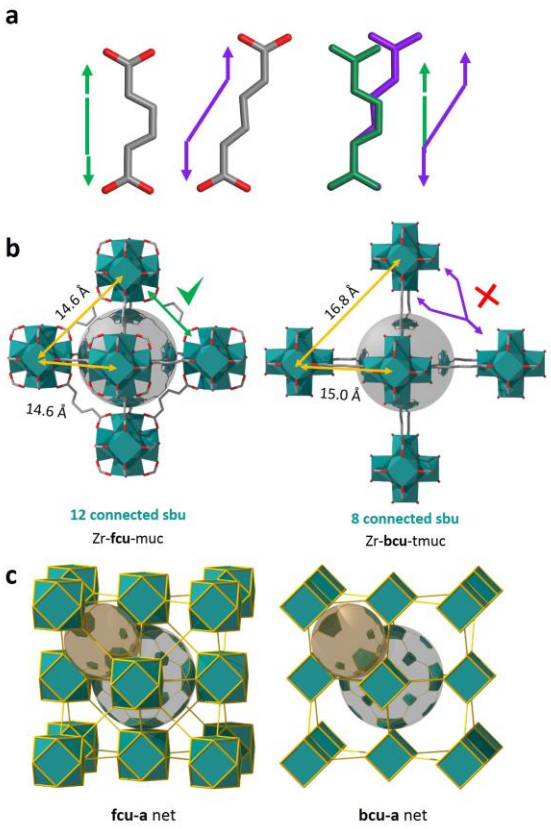


Figure 2. a) View of the two conformations adopted by tmuc in Zr-**fcu**-muc (linear; green) and Zr-**bcu**-tmuc (zigzag; purple). b) Comparison of the regular octahedral cage in Zr-**fcu**-muc, in which all cluster distances are equal, and the distorted octahedral cage in Zr-**bcu**-tmuc, in which longer distances correspond to ligand voids. c) Comparison of **fcu-a** and **bcu-a** networks.

We prepared single crystals of the isoreticular Zr-**bcu**-MOFs Zr-**bcu**-26ndc, Zr-**bcu**-22bipy44dc, Zr-**bcu**-azo33 by using similar conditions as for Zr-**bcu**-tmuc but replacing tmuc with either 26ndc, 22bipy44dc or azo33, respectively. For each synthesis, the reaction time and the amount of modulator were slightly adjusted to optimize crystal quality (see Supporting Information). As expected, SCXRD analysis confirmed the formation of the targeted family of isoreticular Zr-**bcu**-MOFs (Figure 1c,d, Figures and Tables S2-S4).

Due to the similar height of the three ligands, the general dimensions of the resulting MOFs were governed mainly by the width (*i.e.* the transversal parameter) of the corresponding zigzag ligands. In fact, their cell parameter values were in strong agreement with the theoretical values obtained with the equations extracted from the parent model structure of Zr-**bcu**-tmuc (*vide supra*), as illustrated in Figure 3 and in Table S5. Thus, the *a* and *b* cell dimensions, and the pore size, increased with increasing width: 17.5 and 7.3 Å (*a* and *b* value and pore size) for Zr-**bcu**-26ndc; 21.2 and 9.8 Å for Zr-**bcu**-22bipy44dc; and 22.2 and 12.0 Å for Zr-**bcu**-azo33 (Figure 1d). Contrariwise, the *c* parameter (or cluster-to-cluster distance) decreased with increasing width: 22.6 Å for Zr-**bcu**-26ndc, 18.9 Å for Zr-**bcu**-22bipy44dc and 15.8 Å for Zr-**bcu**-azo33 (Figure 3).

In summary, we have reported a new design approach to access novel isoreticular MOFs based on disrupting the collinearity of the carboxylate groups in 2-connected ligands. Our work has revealed that the transversal parameter in organic ligands can be modulated for reticular synthesis of MOFs, as demonstrated in our rational synthesis of four isoreticular Zr-**bcu**-MOFs using zigzag ligands. This parameter provides an additional degree of structural fine-tuning in MOFs by reticular chemistry, enabling deviations from default structures such as the **fcu** topology typically observed for Zr(IV) MOFs with 2-connected, linear ligands. By reducing the connectivity of the inorganic building blocks from the ideal 12 down to 8 to create ordered defects, our approach could become complementary to - or even substitute - the classical monotopic ligand (modulator) addition for MOF synthesis.

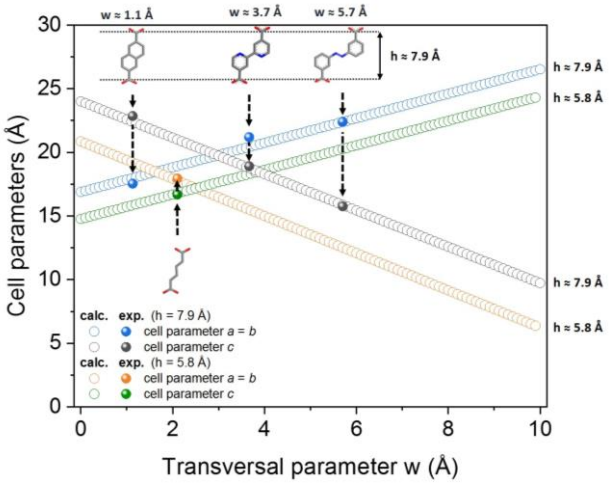


Figure 3. Comparison of the theoretical parameters *a*, *b* and *c* for the Zr-**bcu**-MOFs, with the experimental values for height: 7.9 Å (Zr-**bcu**-26ndc, Zr-**bcu**-22bipy44dc and Zr-**bcu**-azo33) or 5.8 Å (Zr-**bcu**-tmuc).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b07050.
Detailed synthesis, structural data, FTIR spectra, PXRD diagrams, TGA curves and adsorption data.

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Notes

The authors declare no competing financial interests.

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